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INVESTIGATION OF THE COMBUSTION OF FUEL OIL WITH A VANADIUM-CONTAINING ASH

[Issledovanie szhiganiya mazuta s vanadiysoderzhashchimy zoloy]

by

V. N. Abramov, S. I. Ofitserov, V. I. Khmyrov

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Experience in the industrial operation of boiler units and gas turbines, which run on heavy fuel oil, shows that the available research on the composition of the ash residue contained in heavy fuel oil, on the effect of separate components on the melting point of the ash, and the residue's ability to form deposits and cause corrosion of materials, does not make it possible to unequivocally judge the effect of various factors on the process of formation of deposits and the intensity of corrosion.

Analysis of the data available in the literature shows that, at present, the regularity of behavior of the elements of the ash residue in a gas flow, and particularly the dependence of the properties of the ash residue on the operating conditions of the combustion chamber, have been studied to an insufficiently complete

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extent. The absence of such data does not make it possible to establish well-founded requirements both for the structure and for the operating conditions of combustion chambers designed for the burning of heavy fuels.

It is well-known that vanadium is one of the most active elements of ash residue, insofar as corrosion and deposits are concerned. Therefore, only the behavior of vanadium is examined in the present study.

During combustion of a fuel, oxidation of vanadium takes place, and, from the bivalent state in which it is found in the crude oil, the vanadium will change into tri-, tetra-, and pentavalent states, forming the oxides V_2O_3, V_2O_4, and V_2O_5 in the liquid or solid state, and the gas phase V_4O_{10}.

The basic portion of the vanadium is found in the high-molecular asphalt-resin fraction of the crude oil as organo-metallic compounds of complex structure [1]. Therefore, during combustion of a drop of the fuel, the vanadium will be concentrated in the coke residue, the combustion of which is evidently the basic stage of the process which has the greatest effect on the properties of the soot which forms.

We will examine the oxidation reactions which are possible during the combustion of the coke residue:

1. $2C+O_2=2CO$;
2. $C+O_2=CO_2$;
3. $2CO+O_2=2CO_2$;
4. $4VO+O_2=2V_2O_3$;
5. $2VO+O_2=V_2O_4$;
6. $^4/_3VO+O_2=^2/_3V_2O_5$;
7. $^4/_3VO+O_2=^1/_3V_4O_{10}$;
8. $2V_2O_3+O_2=2V_2O_4$;
9. $V_2O_3+O_2=V_2O_5$;
10. $V_2O_3+O_2=^1/_2V_4O_{10}$;
11. $2V_2O_4+O_2=2V_2O_5$;
12. $2V_2O_4+O_2=V_4O_{10}$;
13. $2V_2O_5=V_4O_{10}$.

We took the changes in the standard isobaric-thermodynamic potentials, for the reactions of forming compounds from elements, from the tables in [2]. For all the other reactions, the changes in isobaric potentials were computed by the combining method based on the additivity of isobaric potentials, and calculated for 1 mole of oxygen.

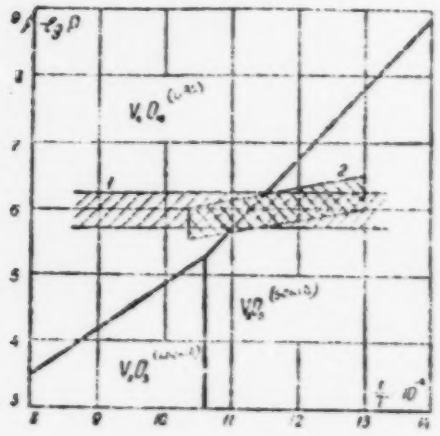

Fig. 1. Dependence of the partial pressure of vanadium pentoxide on temperature: 1-in boilers, $\alpha \cong 1$; 2-with expansion in a turbine.

The change in the isobaric potential for reaction 13 is obtained on the basis of the data on the pressure of vapors of liquid vanadium pentoxide.

There are several formulas in the literature for the determination of the partial pressure of vanadium pentoxide. The data of A. Yu. Polyakov are considered the most complete, although they are somewhat overstated, since the effect of thermodiffusion and change in composition of molecules in the vapor phase was not taken into account in the experiment. The diagram given in figure 1, constructed according to the formula of Kubashevskii and Evans [3], was obtained on the basis of the data of A. Yu. Polyakov, taking into account the effect of thermodiffusion and change in composition of molecules in the vapor phase on the liquid vanadium pentoxide [4]:

$$2V_2O_{5\,\text{liquid}} \longrightarrow V_4O_{10\,\text{gas}}.$$

We did not encounter experimental data in the literature on the pressure of the vapor of vanadium pentoxide below its melting point. Therefore, in figure 1, this dependence is constructed according to the formula obtained by means of extrapolation of Polyakov's data into the realm of a solid pentoxide, with consideration for the melting heat of 15,560 cal/mole. The corresponding formulas of this dependence have the form:

$$\lg P_{atm.} = -\frac{10500}{T} + 5{,}77 \quad (T \leqslant 943^\circ K);$$

$$\lg P_{atm.} = -\frac{7100}{T} + 2{,}17 \quad (T > 943^\circ K).$$

From the last formula, we find the change in the isobaric potential for the process of evaporation of liquid vanadium pentoxide

$$\Delta Z_{13} = 32\,480 - 9{,}928 \cdot T.$$

Given in figure 2 are the data on the change in isobaric-thermodynamic potential for the 13 reactions enumerated above. Based on them, it is possible to assess the depth of occurrence of the reactions we are interested in. Given below are the results of the calculation of the combined occurrence of reactions 2 and 7.

$T, ^\circ K$	P_{CO_2}, abs. atm.	$P_{V_2O_{10}}$, abs. atm.
1000	0,014	$2{,}5 \cdot 10^{-23}$
1000	0,14	$3{,}2 \cdot 10^{-20}$
1800	0,014	10^{-22}
1800	0,14	10^{-19}
2500	0,014	$2 \cdot 10^{-22}$
2500	0,14	$2 \cdot 10^{-19}$

As is evident, the possibility of the change of VO into the vapor phase V_4O_{10} depends strongly on the completeness of the reaction of combustion of the carbon, and on the fact that the VO fraction, having changed into V_4O_{10}, is a quite negligible magnitude, as compared with the partial pressure of V_4O_{10} vapors which is capable of forming during the total evaporation of the V_2O_5 from an ash particle at a pressure of 1 abs. atm. and $\alpha = 1$. Thus, with a vanadium pentoxide content of 120-350 mg/kg of fuel, the partial pressure of the V_4O_{10} vapors is $0.65 \cdot 10^{-6}$—$1.9 \cdot 10^{-6}$ abs. atm., respectively. With the combined occurrence of reactions 2 and 10, or 2 and 12, the outflow of the vapor phase of V_4O_{10} is even less.

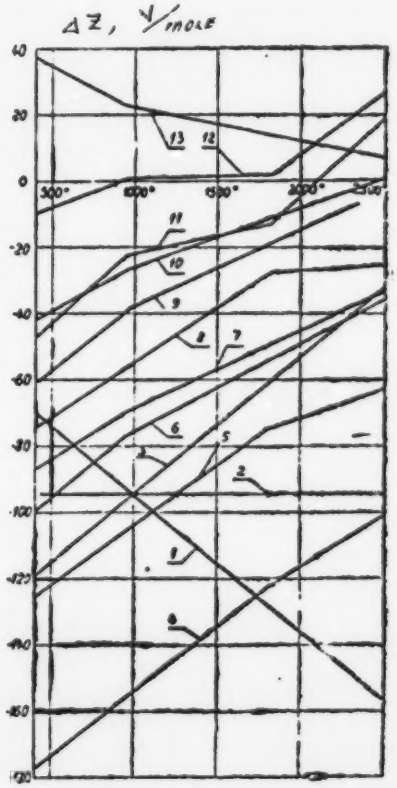

Fig. 2. Change in isobaric-thermodynamic potential for combustion reactions of carbon and oxidation reactions of vanadium (T, °K).

Calculations show that the outflow of vanadium pentoxide into the vapor phase prior to completion of the burn-up of the carbon is so slight that it can be disregarded. However, the comparison of the given data [2] on the pressure of VO vapor with the vanadium content in fuel oil attests to the fact that, at

temperatures above 2000 °K, all of the VO is capable of changing into the vapor phase, i.e. the process $VO_{sol} \longrightarrow VO_{gas}$ will take place simultaneously with the burn-up of the carbon. With the presence of ashes in the interior of a furnace, with a temperature above 2000 °K, this process can show an effect on the formation of an ash residue.

The absence of thermodynamic data on VO_{gas}, and other vanadium compounds in the vapor phase, does not provide the opportunity of tracing the subsequent transformations of the VO_{gas}. Therefore, it is not known what kind of effect the process of VO vaporization can have on the process of the occurrence of vanadium corrosion. In the case of the oxidation of VO_{gas} to V_4O_{10}, the process $VO_{sol} \longrightarrow VO_{gas}$ will promote a reduction in the possibility of the occurrence of vanadium corrosion. Otherwise, VO can condense and oxidize to V_2O_5 on surfaces having a temperature below 2000 °K.

Vanadium, remaining in an ash particle as VO or V_2O_3, subsequently changes into V_2O_4, and is finally oxidized to V_2O_5. The final composition of the oxide will be determined by the parameters of the system after the completion of the combustion process, i.e. by the partial pressure of the oxygen and the temperature. Given in figure 3 are the results of the calculation of the composition of the oxide in an ash particle as a function of the combustion conditions of the fuel [5].

The formation of the vapor phase V_4O_{10} continues, according to reactions 10 and 12, along with the formation of oxides in a liquid or solid state. The composition of the products of com-

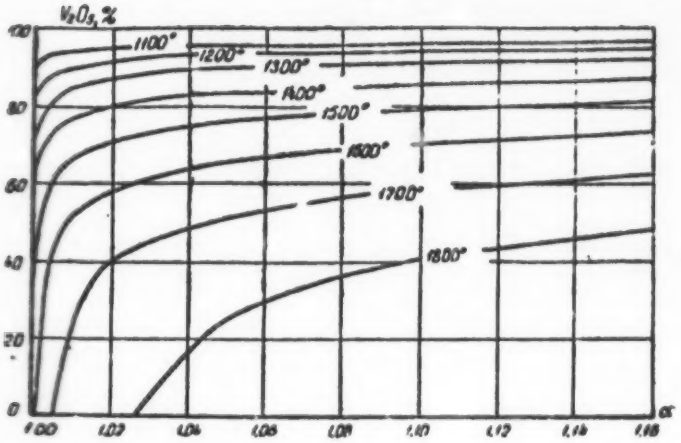

Fig. 3. Dependence of the equilibrium content of vanadium pentoxide in the oxide on the air surplus α in the combustion zone for various temperatures (°K).

bustion (oxygen content in them) shows a large effect on the course of these reactions. The examination of the conditions of occurrence of these reactions with extremely low air surpluses is of the most interest, since with $\alpha > 1.02$, there is considerably more oxygen in the combustion products than is necessary for the complete change of the vanadium contained in the fuel oil into the vapor phase V_4O_{10}.

For the analysis of the occurrence of reactions 10 and 12 with $\alpha = 1$, it is necessary to examine the combined equilibrium of reactions 10 and 3, and 12 and 3:

$$\Delta Z_3 = \Delta Z^0_3 + 4{,}575 \cdot T(2\lg P_{CO_2} - \lg P_{O_2} - 2\lg P_{CO}),$$

$$\Delta Z_{10} = \Delta Z^0_{10} + 4{,}575 \cdot T(1/2 \lg P_{V_4O_{10}} - \lg P_{O_2}).$$

$$\Delta Z_{12} = \Delta Z^0_{12} + 4{,}575 \cdot T(\lg P_{V_4O_{10}} - \lg P_{O_2}).$$

From the condition $\Delta Z_3 = \Delta Z_{10}$, we find for reaction 10

$$\lg P_{V_4O_{10}} = 2 \cdot \left(\frac{\Delta Z_3^\circ - \Delta Z_{12}^\circ}{4{,}575 \cdot T} + 2 \lg \frac{P_{CO_2}}{P_{CO}} \right),$$

and from the condition $\Delta Z_3 = \Delta Z_{12}$, for reaction 12

$$\lg P_{V_4O_{10}} = \frac{\Delta Z_3^\circ - \Delta Z_{12}^\circ}{4{,}575 \cdot T} + 2 \lg \frac{P_{CO_2}}{P_{CO}}.$$

The ratio $\frac{P_{CO_2}}{P_{CO}}$ was calculated according to the equilibrium constant of reaction 3, from the condition of dissociation of CO_2 at a partial pressure of 0.14 atm.

Calculations, according to the equation for reaction 10, show that vanadium can change completely from an ash particle to the vapor phase as V_4O_{10} in the temperature interval from 1000-2500 °K, and for reaction 12—at temperatures above 1180-1260 °K (fig. 4). The lower limit of the temperature corresponds to a vanadium content in the fuel oil of 120 mg/kg of fuel, and the upper limit—350 mg/kg (scaled for V_2O_5).

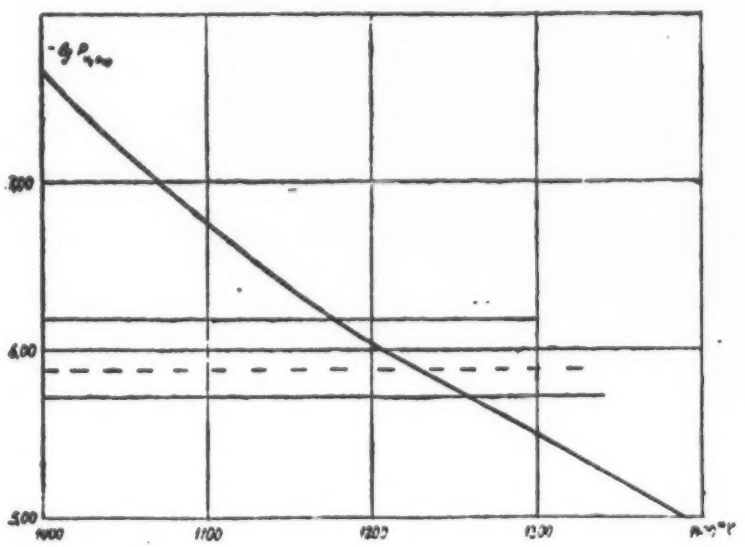

Fig. 4. Dependence of the partial pressure of V_4O_{10} on temperature with α = 1.00.

Similar calculations, carried out for an air surplus corresponding to $\alpha = 1.01$, attest to the fact that, in the temperature range from 1000 to 2500 °K, the reactions examined above can proceed up to complete vaporization of all the vanadium contained in the fuel, with the formation of the vapor phase V_4O_{10}.

As a result, one can assume that an ash particle, forming during the complete combustion of carbon in a high-temperature zone, does not contain vanadium, while an ash particle which contains vanadium can only form during the burn-up of coke in a low-temperature zone (for example, on the surface of boiler pipes).

The data of thermodynamic research on the formation of V_4O_{10} vapors reflect only the qualitative picture of the possible nature of the flow of the reactions since the pressure of saturated V_4O_{10} vapors, as well as the rate of evaporation of the liquid pentoxide, depend on the composition of the oxides which form the ash particles, and on the products of combustion. However, this information is not conclusive (only of qualitative nature), and it is not possible to utilize it for calculations.

Nevertheless, thermodynamic analysis of the processes of oxidation and vaporization of vanadium oxides from ash particles during combustion of fuel oils indicates two possible methods of decreasing the complications associated with the formation of liquid vanadium pentoxide.

The first method is characterized by the most complete removal of vanadium from ash particles by means of high-temperature treat-

ment of the volatile ash.

During the combustion of domestic fuel oils, there are not conditions for the condensation of vanadium pentoxide in drops under the operating conditions of both boilers and gas turbines. The precipitation of vanadium pentoxide from the vapor phase can occur only at temperatures below the melting point of the pentoxide. In this case, vanadium pentoxide already can not represent a danger for the material of the working surfaces.

The second method is associated with the retention of vanadium in the ash particle in the form of an elementary oxide by means of combustion of the fuel oil with extremely low air

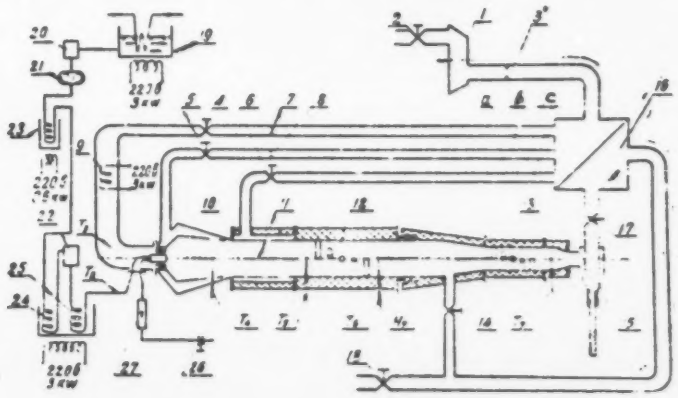

Fig. 5. Schematic of the experimental unit: 1-blower; 2,4,5,6,14,17,18-throttle control gates; 3,7,8-throttle measuring discs; 9-heater of initial air; 10-combustion chamber; 11-burn-up chamber; 12,13-sample chambers; 15-cyclone ash trap; 16-heat exchanger; 19-fuel tank; 20,22-fuel-cleaning filters; 21-fuel pump; 23,24,25-coil fuel heaters; 26-air reducer; 27-rotameter.

surpluses, and is successfully realized in practice during the combustion of fuel oil in the fire boxes of boilers [6]. This

method is not applicable for the conditions of a gas-turbine unit (GTU) or in the presence of drafts in boilers, since the elementary oxides of vanadium, getting onto working surfaces, can oxidize further, in the zone with increasing surpluses of air, up to a pentoxide. Therefore, the process of fuel combustion under conditions which are favorable from the point of view of formation of the vapor phase V_4O_{10} ought to be considered the most general-purpose method.

Experiments on the study of the processes of the formation of deposits and of changes in the composition of the ash residue of the solid phase of the combustion products during the combustion of fuel oils were conducted in a special unit (fig. 5).

Fuel oil, comparable in its characteristics to grade M-100, was utilized for the tests. The ash content was 0.1%, the vanadium content—12% of the weight of the ash (or 260 mg of V_2O_5 per 1 kg of fuel).

The fuel was injected by a high-pressure pneumatic nozzle, which made it possible to change the type of fuel injection within wide limits without changing its consumption or the fuel: air ratio in the combustion zone.

For the exclusion of the effect of transient and non-stationary processes, the samples used for the study of deposit formation were manufactured as movable. During the start-up of the unit and the adjustment of the conditions, the samples were located in the recesses of bushings, and were introduced into the flow after emergence into a stationary set of conditions.

Prior to a change in conditions or the end of a test, the samples were again removed from the flow.

The removal of the solid phase of the combustion products from the settling reservoir of the cyclone ash trap was carried out at equal time intervals (20 minutes) throughout the experiment. In this way, reliable control was ensured over the stationariness of the process, since all of the changes in the operating conditions of the unit were fixed, first and foremost, according to the amount of collected solid phase.

The conditions in the combustion zone corresponded to the working conditions of a GTU combustion chamber. The air surplus in the zone, from the register to the first mixer, was recorded within the limits of α = 0.97-1.1, and in the zone from the first mixer to the second mixer—within the limits of α = 1.7-2.3. In the zone where the samples were located, at a flow temperature of 800°, the air surplus was $\alpha \approx 3.5$, because of large relative losses into the surroundings (low fuel consumption).

During the investigation of the process of deposit formation, the weight, form, and nature of adhesion to the surface of the metal were determined. The amount of the deposits was determined by the actual coefficient of adhesion, which is the ratio of the weight of the deposits to the conditional weight of the ash arriving at the midsection of the sample during the test. For visual evaluation of the nature of the deposits, the samples were photographed both with a "Zenith" camera using extension rings, and through a microscope.

The properties of the solid phase were studied according to the following guidelines:

1) the total amount of collected solid phase, and the amount of the solid phase attributed to the amount of fuel consumed during the selection time, were determined;

2) the particles of the solid phase were separated into several fractions by size;

3) the carbon and vanadium contents in the ash of each fraction were determined.

Several series of tests were conducted in the experimental unit, in each of which only one factor was variable.

For the investigation of the process of deposit formation, three different configurations of the stage II mixer, differing from each other in the means of air supply to the combustion zone, were utilized (fig. 6). In tests with mixers of all types, coke did not form on the thermocouple or on the samples. In connection with the fact that the organization of the combustion zone according to configuration a did not permit the control of the temperature level in it, combustion chambers were manufactured with a separate air supply to the register and the stage I mixer, as well as stage II mixers of different lenghts with all air supply into one row of apertures (configurations b and c).

Presented in figure 7 are the results obtained in this series of tests. It was established that the distance from the combustion zone to the point where the samples were located had a substantial effect on the amount of deposits and their composition.

The amount of deposits on the sample and the vanadium content in the deposits decrease in proportion to the distance of the sample from the combustion zone. The most intense change in the amount of deposits and in their composition is observed in a section located close to the combustion zone. These sections also exist for stage II mixers of types a and b. The first samples in the unit with a stage II mixer of type c were located at a distance from the combustion zone greater than the length of the zone of

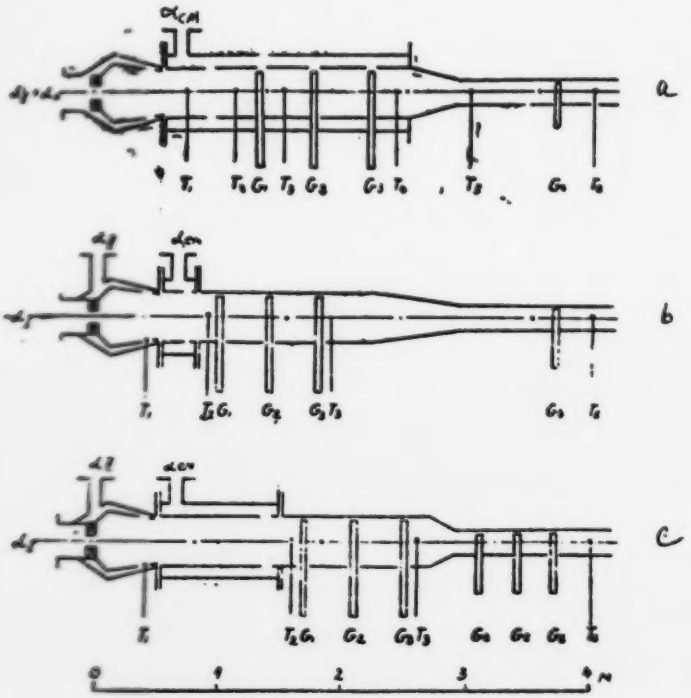

Fig. 6. Diagram of placement of thermocouples and samples in the unit with different stage II mixers: a-stage II mixer with air delivery in stages through several rows of apertures, the temperature changes smoothly from T_{comb} to T_{flow}; b-stage II mixer with supply of all air through a single row of apertures, length of mixer is ~ 300 mm; c-stage II mixer with supply of all air through a single row of apertures, length of mixer is ~ 1000 mm.

intense change in the amount of deposits. Therefore, the decrease in the amount of deposits on the first samples with mixers of configurations a and b can be explained by the change of the particles from a gummy, "pitchy" state to a "dry" state, especially since the vanadium content in these deposits is the same as in the ash obtained during the evaporation of fuel oil.

Subsequent reduction in the intensity of increase of the deposits accompanied by a continuing reduction in the vanadium content in them can be explained only on the basis of the hypothesis on the evaporation of vanadium from an ash particle. The possibility of the evaporation of the vanadium from a particle is proved by thermodynamic calculations.

There is information in the literature [7], which was also supported by our research, on the dependence of the melting point of ash residue on the vanadium content in it. The change in the amount of the deposits and the vanadium content in them can be schematically represented in the following manner: the portion of the vanadium evaporating from the particle increase in proportion to the increase in the time that the particle is located in the flow. Here, the melting point of the particle increases and, accordingly, decreases its ability to stick to the sample. The vanadium content in the particles of the trapped solid phase was always low.

Thus, the obtained results make it possible to assume that the forming deposits are determined, to a significant degree, by the composition of the solid phase particles at the moment of their

depositing onto the samples, and that the composition of the particles of the solid phase depends both on the conditions and on the time that the particles are located in the combustion zone.

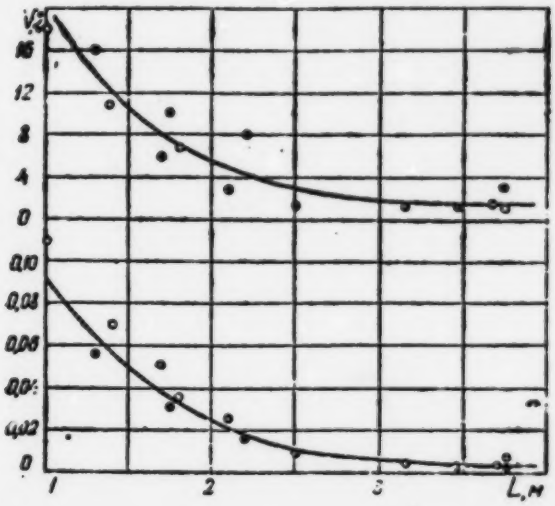

Fig. 7. Change in the amount of deposits and the content of vanadium in them according to the length of the gas channel.

Investigations of the dependence of the amount of deposits and the characteristics of the solid phase on the coefficient of air surplus in the combustion zone ($\alpha_I + \alpha_{II}$) were conducted in a unit with a stage II mixer of configuration c with the most complete burn-up of the fuel (fig. 8).

As is evident from the figure, with an increase in the air surplus in the combustion zone $\alpha_I + \alpha_{II}$ = 1.8-2.3 (α_I was maintained within the limits of 0.97-1.1 in all of the tests), the amount of deposits on the samples increased, and the completeness of the fuel burn-up, recorded according to the amount of trapped solid phase and the carbon content in the trapped particles, decreased. With an increase in the amount of deposits, the portion of vanadium

they contained increased. Simultaneously, with a reduction in the completeness of burn-up of the fuel particles, the amount of vanadium increased.

The increase in the completeness of fuel burn-up, with a reduction (within the indicated limits) in the amount of air supplied to the combustion zone, agrees well with the well-known fact of the most intense combustion of fuel with a surplus of air in the combustion zone $\alpha_{comb} = 1.4\text{-}1.7$.

The obtained dependence of the ash composition on the air surplus in the combustion zone is analogous to the results of thermodynamic research. With a decrease in the air surplus, under our conditions, the length of the high-temperature zone increased and, for a constantly larger portion of the fuel, conditions were created which were favorable for the evaporation of vanadium from the particles.

The comparison of the data in figure 7 on the dependence of the composition of the deposits on the mounting point of the samples with the data of figure 8 on the dependence of the ash content on the completeness of the burn-up of the fuel particles shows that the more complete the burn-up of the fuel, the less vanadium there is in the ash residue and in the deposits.

A similar dependence was obtained with the investigation of the composition of the ash residue of the particles obtained by the division of the trapped solid phase into fractions: the smaller the size of the coke particles (i.e. the smaller the drops they were obtained from), the less vanadium there was in

them.

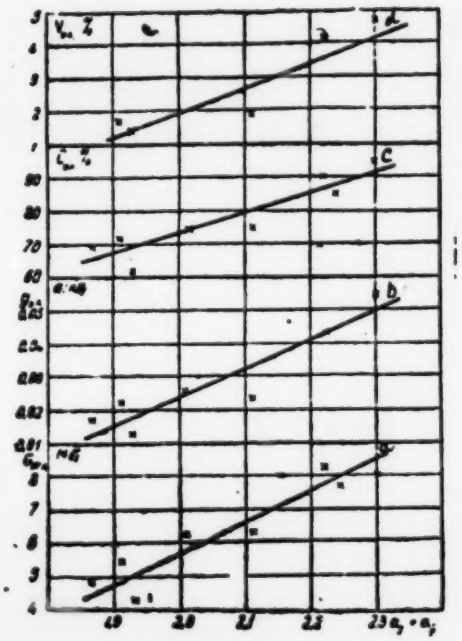

Fig. 8. Dependence of the amount of the deposits and the nature of the solid phase on the coefficient of air surplus in the combustion zone ($\alpha_I + \alpha_{II}$): a-amount of deposits on samples; b-amount of solid phase trapped in the cyclone ash-trap; c-carbon content in the solid phase; d-vanadium content in the ash residue of the trapped solid phase.

For the exclusion of various types of subjective errors, which occur during the manufacture of preparations and the conducting

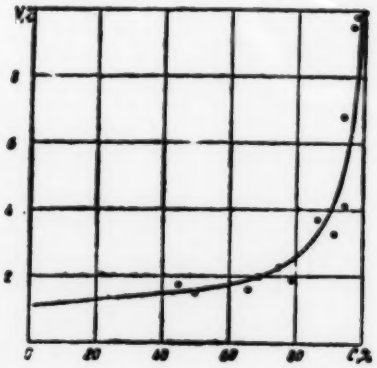

Fig. 9. Dependence of the portion of the vanadium in the ash residue of the solid phase particles on the carbon content in the particles.

of analyses, several weighed quantities of the trapped solid phase, obtained in the tests under different conditions in the combustion zone and with different types of fuel injection, were taken. All of the weighed quantities were united into several groups, which differed in the carbon content in the particles, and were ashed simultaneously under one or another set of conditions. The vanadium content in the particles was determined using a spectro-

photometer. The clear-cut dependence between the vanadium content in the ash residue and the completeness of fuel burn-up, characterized by the carbon content in the particles, is shown in figure 9. Thus, the hypothesis that, during the burn-up of fuel, conditions are created when the vanadium contained in the ash residue can change into the vapor phase, is corroborated.

The obtained experimental data agrees well with the conclusions drawn on the basis of thermodynamic calculations.

Thermodynamic research on the processes of oxidation and vaporization of vanadium during the simultaneous occurrence of fuel burn-up attests to the possibility of creating conditions in the combustion zone such that the vanadium contained in the fuel can change completely into the vapor phase as V_4O_{10}.

It has been established that there exists a quite definite dependence between the conditions in the combustion zone, the degree of completion of the burn-up process of the fuel particles, and the composition of the ash residue: the more completely the fuel burned in the zone of high temperature, the less vanadium in the ash residue and the less danger of the formation of deposits and the appearance of high-temperature (vanadium) corrosion.

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